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Surface modification of polypropylene (PP) using single and dual high radio frequency capacitive coupled argon plasma discharge

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ABSTRACT

Single (40.68 MHz) and dual (40.68/2.1 MHz) high radio frequency (RF) argon plasma discharge was employed as a source of a low-temperature treatment mechanism that was used to modify the surface of polypropylene (PP). The effects of argon plasma on the surface chemistry and the surface morphology of PP were studied using X-ray diffraction analyses. In this study, samples were treated under different plasma operation conditions for parameters such as RF power, gas pressure and treatment time. Furthermore, the crystallite size was calculated (using Scherrer equation) from the diffraction pattern of the β fraction (Full Width at Half maximum) for PP samples. The results reveal that the crystallite size strongly increases with RF power and treatment time, but decreases with gas pressure. From the analysis, it was found that the treated samples have higher crystallite sizes in compared to those of the single RF plasma discharge. This happens because the increase of plasma temperature leads to increases in the crystallization of PP sample, so that the crystallite size also increases. Furthermore, because of the advantageous features of the dual-RF plasma mode, the surface modification of PP sample can occur more quickly than is possible via the single-RF plasma discharge.

1. Introduction

Polypropylene (PP) is a biomaterial that is extensively used in syringes, surgical sutures, catheters, blood transfusion bags and hemodialysis membranes [1,2]. Moreover, the mechanical properties and lower thermal conductivity of PP lead to its use in food-packing industry. Conversely, its biomedical applications are restricted due to low surface polarity and hydrophobic nature, in spite of its good mechanical properties and lightweight [3]. For these reasons, it is very important to modify the surface properties of PP without changing its bulk properties [4,5]. Therefore, plasma discharge treatment is one of the best treatment methods, as plasma interacts with the polymer surface and not with its bulk. The interaction typically occurs via physical activation followed by chemical reactions: Electrons, ions, photons, and free radicals interact with a polymer surface via processes that leads to heating and then breaking of chemical bonds to prepare the surface for the reaction. The combinations among the chemical groups then occur in the plasma environment [6]. Consequently, researches have used several surface modification techniques to change the properties of PP, such as flame treatment, corona discharge and UV irradiation [7–9]. However, the interest in low-temperature high frequency capacitively coupled plasma discharge was increased because of the possibility of modifying a wide list of natural and synthetic polymers without significant changes in their molecular structures [10]. The main advantage of this versatile technique is that it is confined to the surface layer of a material and dose not affect its bulk properties. Moreover, it is a clean, fast, dry and time-efficient process with a large variety of controllable process parameters (e.g. discharge gas, power input, pressure, treatment time). In this process, the gaseous molecules are excited to energetic states while their kinetic temperature remains close to room temperature [11,12].

Different studies have explored the use of different gaseous plasma discharge techniques for the surface modification of polymers. One of these studies used reactive gas plasma to add new chemical functionalities to the exposed layers that where accompanied by small morphological changes, in contrast to the most intense surface deterioration mechanisms that exist with inert gas plasmas [13]. Furthermore, surface functionalization of PP surfaces under different plasma operation conditions (e.g. low-pressure and high-pressure plasma, RF power, and exposure time) was investigated, with the resulting surface characteristics (surface polarity, permeability, adhesion, etc.) were indexed [14–16].

During low-pressure plasma treatment, many free radicals can be created on the surfaces of materials if an inert gas (such as argon) is employed as a process gas. Therefore, the argon gas plasma discharge treatment (as observed previously) creates new

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surface morphologies and is more efficient in introducing oxygen-containing groups with relatively low surface roughness [17,18]. These polymeric surfaces are usually not wettable and have poor adhesions. Nevertheless, after plasma treatment the surface energy increases, with accompanying enhancement of wettability and adhesion. Consequently, PP is strongly hydrophobic due to the lack of polar functional groups on the polymer chains. However, plasma treatment changes the surface properties and the contact angle [19,20]. Among many kinds of polymers, hydrophilicity of the PP surface shows the best improvement after plasma treatment due to decreases of the contact angle [21]. In other words, the plasma treatment increases the hydrophilicity of PP and provides better contact with aqueous solutions, indicating that the argon plasma discharge decreased the contact angle of PP [22]. In addition, PP samples after plasma treatment (thermal processing)have a higher crystallinity degree and orientation compared to the untreated PP sample. Meanwhile, the crystallinity determination was performed previously by terahertz time domain spectroscopy (THz-TDS), with which it was observed that the degree of crystallinity was lower for untreated samples than for treated samples [23]. Polypropylene with a high crystallinity leads to increases in hardness, strength, and wear resistance. However, low-crystallinity PP is associated with good ability to be processed and better transparency.

In this study, as will be explained in the sections below, the crystallite size increased almost 90% in comparison to its value for a reference sample when the exposure time and RF power were increased. Consequently, polymers can acquire new combinations of properties after exposure to non-equilibrium low temperature single high frequency CCP discharge plasma [24,25].

In general, the cold plasma is partially ionized gas composed of highly excited atomic, molecular, ionic and radical species with free electrons and photons. Although the electron temperature can be much higher, the bulk temperature (gas temperature) is essentially the ambient one (300 K). Plasma can be generated between electrodes in low- and high-frequency devices – typically 40 kHz, 13.56 MHz, respectively – or with microwave generators (2.45 GHz) [27,26]. In addition, a newer method has been advised with dual high/low (40.68/2.1 MHz) frequency generators [28].

It is well known that direct electron and ion flow is the most reactive component in the plasma reactors. Thus, the thermal effect of the ion recombination makes the basic contribution to modification of the polymers. Following this, in this study we attempt to use a new concept for low-temperature plasma processing (dual high radio frequency CCP) to make the effect of the ions more powerful, controllable, and faster. The main principle of this reactor, as previously described [29,28], is that the ion can be controlled by the high-frequency (HF) generator (40.68 MHz), while the low-frequency generator (LF) (2.1 MHz) mainly determines the ion energy. Therefore, we believe that this technique will contribute to development a new method for surface treatment of many materials.

X-ray diffraction is a convenient method for determining the mean size of nano-crystallites in non-crystalline bulk materials. Thus, XRD is used to identify crystalline phases and orientation. In addition, XRD can be used to determine the atomic arrangement and structural properties of these materials. In general, PP has three common phases (α-, β-, and γ-phase), but the monoclinic α-phase is the most frequently observed structure of PP and is usually obtained upon crystallization from the melt or from solution. Under certain conditions (such as the different temperature gradients), the formation of the hexagonal β-modification is predominant. On the other hand, the less common triclinic γ-phase occurs only under high pressure and shear during the crystallization process. However, after thermal treatment, this modification transforms into the stable α-phase, which is the dominant phase of this study. Therefore, the best way to determine the transformation between these phases is via XRD [30–32].

The average crystallite size was calculated using the following well-known Scherrer formula [33]:

$$\text{Crystallite size} = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the X-ray wavelength in nanometer (nm) (0.154 nm for Cu-Kα), β is the peak width of the diffraction peak profile at the half maximum height (FWHM) resulting from small crystallite size in radians and k is a constant related to crystallite shape, normally taken as 0.9, with an average = 1 for polymers. The value of β in 2θ axis of the diffraction profile must be given in radians. The θ can be in degrees or radians, since the *cos*θ corresponds to the same number. Since, the crystallite size in polymers is usually on the nanoscale in the thickness direction. The size of crystallites can be determined using variants of the Scherrer equation. Application of the Scherrer equation involves taking the peak full-width half-maximum (FWHM), removing the instrumental broadening and then assuming that all remaining broadening is caused by particle size effects alone. The average crystallite size was determined by the mean of fitting a Gaussian–Lorentzian curves to the four most intense reflections peaks (110), (040), (130) and (111) and measuring the full width half maximum and Bragg angle; then these values were used to determine particle size via input into the Scherrer equation [34,35]. Using OriginPro Software (Origin Scientific Graphing and Analysis Software, Version 8.5, 2010), the error bars were determined as the standard deviation from the mean of the fits [36,37].

As can be seen from Eq. (1), peak width due to crystallite size varies inversely with crystallite size: as the crystallite size gets smaller, the peak gets broader. Crystallite size in polymers is usually on the nanoscale in the thickness direction. The size of crystallites can be determined using variants of the above Scherrer equation. As the crystallite size becomes smaller, more crystallites meet the Bragg condition and the radial orientation of these crystallites cover a broader spectrum of angles.

The purpose of this study is to introduce the advantages of the low-temperature argon single (SF) and dual (DF) high RF-CCP discharge treatment reactor during the modification of the surface of PP under different operational conditions. The structural changes in the physiochemical properties (α-phase crystallite size and peak intensities) of the PP samples induced by the plasma are characterized.

2. Experimental setup

The experimental setup of the single (40.68 MHz) and dual (40.68/2.1 MHz) high radio frequency capacitively coupled plasma discharge has been previously explained [28,29,23]. The polypropylene (PP) samples were supplied by the Department of Chemistry, Middle East Technical University, as well as obtained by extrusion without any kind of additives. PP samples were cut into dimensional rectangular pieces of $10 \times 10 \times 0.1\ \text{mm}^3$. The PP samples were exposured to argon plasma under the following operational conditions: RF power range: 50–200 W, pressure: 0.1–1 Torr, and treatment time: 15–75 min. The system was continuously pumped with two stage oil rotary pump and turbo molecular pumps simultaneously. To avoid atmospheric exposure and achieve more accurate treatment conditions, a load-lock system with sample staging was mounted to the process chamber. The crystallinity data were obtained via X-ray diffraction (XRD) with a Rigaku- MiniFlex. The XRD patterns were used to determine the relative orientation of the crystalline planes [38–40,36,37].